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14. ABSTRACT Vapor grown carbon nanofibers (VGCF) with 60-250nm diameters and 10 to 80µm lengths were blended with the nonpolar organic monomer, dicyclopentadiene, to create liquid dispersions or pastes (based on the wt% fiber used). Ruthenium catalysts were mixed in to cause ring-opening metathesis polymerization, generating tough crosslinked resin matrices reinforced by the nanofibers. In addition to dicyclopentadiene, other liquid resins, including phenolic, epoxies and vinyl esters were also blended with these nanofibers and then cured to form organic matrix carbon fiber composites. When the wt% fiber was sufficient, shapeable pastes could be made, molded and cured. Fluid mixtures could be coated onto surfaces and cured. The dynamic mechanical and mechanical properties and in some cases high temperature erosion resistant properties and electrical properties of the cured composites were measured. VGCF, when blended with EPDA resins, were shown (joint work with S. Phillips et. al. Edwards AFB) to be superb materials for rocket liners in solid propellant motors due high temp. erosion resistance. VGCF-phenolic resins exhibited excellent high temp. ablation resistances in ~1600 °C plasma torch tests, due in part to the short heat transfer lengths of these tiny fibers. As this work proceeded, efforts were broadened to incorporate polyhedral oligomeric silsesquioxane (POSS) nanophases into resins to form oxidation barriers and improve thermal properties. Multifunctional and monofunctional POSS derivatives were incorporated into many resin systems and studies of nanoaggregation were undertaken.					
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INTRODUCTION AND OBJECTIVES

The focus of this proposal is the creation of a variety of composite materials from vapor grown carbon fibers (VGCF) and low viscosity organic matrix resins with an emphasis on the polydicyclopentadiene resin produced by ring-opening polymerization (ROMP) of the low cost and readily available monomer, dicyclopentadiene. The small size and high surface area of VGCF leads to the formation of a paste-like consistency when liquid monomers or preresins are mixed at high shear with VGCF. A wide variety of these pastes were made with DCPD, epoxy, phenolic and vinyl ester resin systems. Following curing, the thermal and mechanical properties of the resulting composites were characterized.

Vapor Grown Carbon Fibers

VGCF are manufactured on a commercial scale by Applied Sciences, Inc. (ASI, Cedarville, Ohio). These fibers are 0.1 to 0.3 μm in diameter and 10-100 μm in length. As produced, the fibers are randomly aligned and on a microscopic scale are found as a tangled matt of intertwined fiber, many of which are curved. The technology to produce the fibers (PyrographTM III) is covered by a licensing agreement between ASI and Delphi Chassis (a division of General Motors). A hydrocarbon gas (methane, natural gas, even coal gas) and a sulfur compound are heated to 1000 - 1200 $^{\circ}\text{C}$ and an aqueous aerosol spray of a metal salt (typically Fe^{+3}) or $\text{Fe}(\text{CO})_5$ introduced. In these reducing conditions iron particles (10^2 to 10^4 atoms) form. These particles act as nucleation points for carbon fiber growth which occurs rapidly as the particles flow downstream with the gas.

Carbon graphitic sheets are formed which wrap around to form multi-walled nanotube fibers. Multiple concentric conical nanotubes grow to lengths of 10 to 100 μm . Continued pyrolysis deposits concentric layers of pyrolytic graphite in an "onion ring-like" geometry over the nanotubes. These fibers approach typical PAN-based fibers in strength and stiffness and have been successfully infused with resin, the VGCF will become extremely attractive for composite reinforcement.

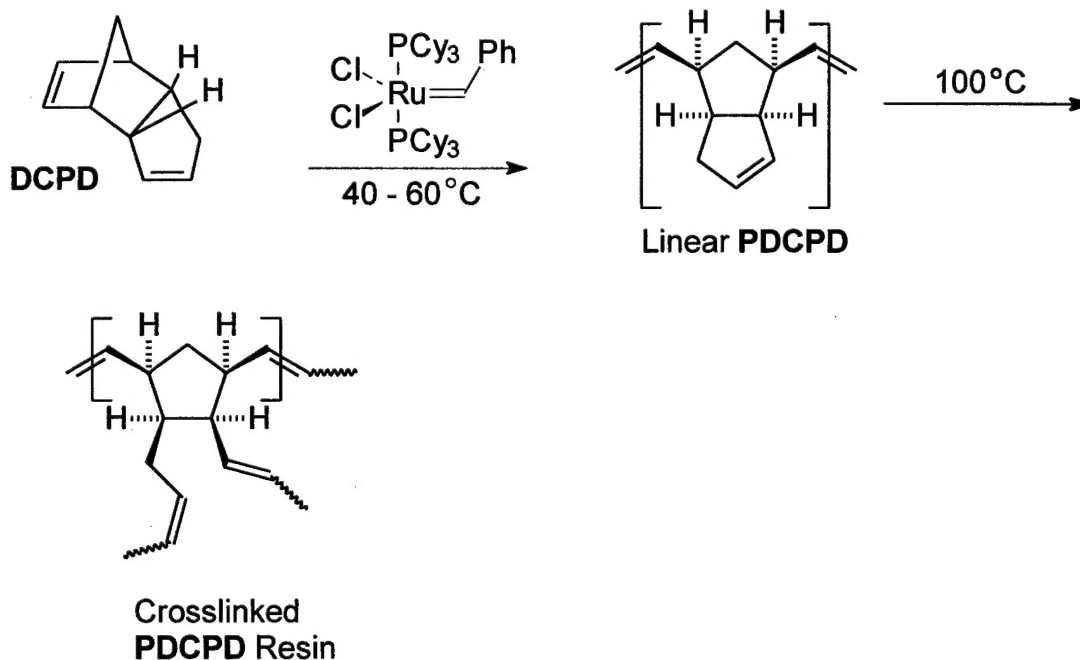
Pittman and Patton obtained the first indirect measurements of the strength and moduli of Pyrograph III from studies of the mechanical properties of VGCF/epoxy composites made from "as-received fibers". The lower limits of their tensile strength (2.5 to 3.4 GPa) and tensile moduli (100 - 166 GPa) were firmly established and most likely values are now thought to be 4 to 5 Gpa and 220 - 300 Gpa ranges, respectively. These values are exceptional considering a high fraction of the fibers used were not straight.

Polydicyclopentadiene (PDCPD). An Advanced Thermosetting Composite Matrix From Low Viscosity Dicyclopentadiene (DCPD).

Advanced Polymer Technology Aerospace, Inc. (APT) has developed a unique ruthenium carbene catalyst system for polymerizing DCPD monomer which is suitable for use in high performance structures and propellant tanks for Kinetic Energy Kill vehicles to meet needs identified by BMDO. These ruthenium carbenes operate in the presence of air, water and a variety of heteroatom containing monomers and polymers. APT originally intended to use PDCPD in low cost chemical and corrosion resistant tanks. However, the unique ability to tailor the polymerization/cure process resulted in cure protocols which produced very tough resins

from low viscosity DCPD monomer. This result suggested that rapid infusion of DCPD, followed by curing at mild conditions, would be advantageous in composite manufacturing. The outstanding properties of cured PDCPD could make this the matrix resin of choice for many high performance composites. This is especially true where composites must be tough, water impermeable, chemically resistant and free of serious residual thermal stresses. Some properties of PDCPD are listed below and the structure of the crosslined polymer is shown.

1. **Tensile strength** (unreinforced) 10,000 psi
2. **High Impact Strength and Toughness** (varieties can be made from 20 to 400 ft. lbs.)
3. **Flexural Modulus** (270,000 to 340,000 psi)
4. **Low Shrinkage During Cure** (0.4% to 2% depending on cure; 1/8th that of epoxies)
5. **Water insensitive during cure.** The resin is totally hydrophobic.
6. **High Hoop Stress** of Glass Fiber Composites (3 times higher than epoxy/glass composites)
7. **Low Viscosity** (most grades of monomer have a viscosity similar to water).
8. **Corrosion Resistant** (virtually impervious to chemicals, withstands oxygen in low earth orbit; surface layer reacts with chlorine or bromine to increase chemical impermeability of the material). If polymerized with a POSS monomer oxidation resistance could be increased.
9. **Low-cost, Good Availability** (various grades available from \$0.50 to \$1.25/lb.; an almost unlimited supply is obtained as biproduct from petroleum refining).
10. **Easily Machined** (as easy as aluminum using conventional machine tools).



Objectives

The low viscosity of DCPD suggested that VGCF could be blended with DCPD to form liquids which could be injected into molds or perhaps performs and cured via processes such as

the SCRIMP process. Higher volume fractions of fibers might blend with DCPD to make pastes which could be shaped prior to curing into net shaped objects. If a high enough fiber concentration could be reached, the cured part might have a low CTR and be machinable. This might also be true of other liquid resin systems such as epoxies, vinyl esters and phenolic resins. Thus, investigations of VGCF/resin composites was undertaken where the resins systems were DCPD, vinyl esters, epoxies and phenolics.

A second objective arose once this project began. Polyhedral oligomeric silsesquioxane (POSS) monomers, first made and polymerized at Edwards Air Force Base, were considered to be a second nanophased material which could be introduced into liquid organic resins followed by curing. The objective was to produce resins with higher thermal stability, greater oxidation resistance, higher Tg and better mechanical properties (strengths, moduli etc.) Thus, POSS monomers produced by Edwards AFB and later by Hybrid Plastics were incorporated into DCPC, phenolic, epoxy and vinyl ester resins.

SIGNIFICANT RESEARCH RESULTS

The work performed under AFOSR Grant No. F49620-99-1-0191 is quite extensive, reaching in many directions. It resulted in 7 refereed journal publications to date and two other manuscripts have been submitted. These are listed below. In addition, 7 invited presentation were given in various forums including SAMPE, NASA-materials, National ACS and IUPAC meetings. Several of these lectures are appearing in published form (abstracts or full papers).

For example, the IUPAC presentation in Ottawa will appear as a published paper in *Macromolecular Symposia* (Wiley VCH) and the POSS Nanotechnology Conference is available, along with every slide presented, on CD.

Finally, a portion of this work done jointly with Edwards AFB as a broad group effort has resulted in a patent application (in preparation by Dr. Blanski, Edwards AFL) in the area of solid rocket propellant liners but this document will be classified. The key research results are listed after the publications.

Refereed Journal Publications Resulting from Research Supported by AFOSR Grant No. F49620-99-1-0191.

1. X. Xu, L. Wang, H. Toghiani and C. U. Pittman, Jr., "Effect of Crosslinking on Mechanical and Viscoelastic Properties of Semiinterpenetrating Polymer Networks Composed of Poly(Vinyl Chloride) and Isocyanate Crosslinked Networks," *J. Applied Polymer Sci.*, **2000**, 78, 1402-1411.
2. C. U. Pittman, Jr., X. Xu, L. Wang and H. Toghiani, "Characterizing Semi-interpenetrating Polymer Networks Composed of Poly(vinyl chloride) and 5-15% of Oligomeric MDI Isocyanate Crosslinked Networks," *Polymer*, **2000**, 41, 5405-5413.
3. C. U. Pittman, Jr., X. Xu, L. Wang and H. Toghiani, "Mechanical and Viscoelastic Properties Semi-Interpenetrating Polymer Networks of Poly(Vinyl Chloride)/Thermosetting Resin Blends," *Polymer Engineering and Science*, **2000**, 40(6), 1405-1413.
4. G. Z. Li, L. Wang, H. Toghiani, T. L. Daulton, K. Koyama and C. U. Pittman, Jr., "Viscoelastic and Mechanical Properties of Epoxy/Multifunctional Polyhedral Silsesquioxane (POSS) Nanocomposites and Epoxy/Ladderlike

- Polyphenylsilsesquioxane (PPSQ) Blends," *Macromolecules*, **2001**, 34(25), 8686-8693.
5. R. D. Patton, C. U. Pittman, Jr. L. Wang, J. R. Hill and A. Day, "Ablation, Mechanical and Thermal Conductivity Properties of Vapor Grown Carbon Fiber/Phenolic Matrix Composites," *Composites Part A: Applied Science and Manufacturing*, **2002** 33(2) 243-251.
 6. G. Z. Li, L. Wang, H. Ni and C. U. Pittman, Jr., "Polyhedral Oligomeric Silsesquioxane (POSS) Polymers and Copolymers (A Review)", *J. Inorg. and Organometallic Polymer*, **2002**, 11(3), 123-154.
 7. G. Z. Li, L. Wang, H. Toghiani, T. L. Daulton and C. U. Pittman, Jr., "Viscoelastic and Mechanical Properties of Vinyl Ester (VE)/Multifunctional Polyhedral Oligomeric Silsesquioxane (POSS) Nanocomposites and Multifunctional POSS-Styrene Copolymers," *Polymer*, **2002** 43, 4167-4176.

Manuscripts Submitted For Publication

1. G. Z. Li, T. Matsuda, A. Nishioka, K. Miyata, Y. Masubuchi, K. Koyama and C. U. Pittman, Jr., "Rheological Properties of Polystyrene. Blends with Rigid Ladderlike Polyphenylsilsesquioxane (PPSQ), submitted to *Polymer* June 6, 2003.
2. G. Z. Li, T. Matsuda, K. Koyama and C. U. Pittman, Jr., "Rheological Properties of Poly(methylmethacrylate)/Rigid Ladderlike Polyphenylsilsesquioxane (PPSQ) Blends, submitted to *Polymer Engineering and Science* in 2002.

Invited Presentations on Research Sponsored by Grant No. F49620-99-1-0191

1. R. D. Patton, C. U. Pittman, Jr., L. Wang, J. R. Hill and A. Day, "Ablative and Mechanical Properties of Vapor Grown Carbon Fiber Composites With Phenolic Matrices," presented at the 24th Annual Conference on Composites Materials and Structures, by the Ceramic, Metal and Carbon Composites Committee (CMC³) of the Advanced Composites Working Group (ACWG) in corporation with the USAF, USA Army, US Navy, DOE, NASA, and DARPA, Jan. 24-28, 2000, Radisson hotel, Cocoa Beach, FL.
2. C. U. Pittman, Jr., R. D. Patton, L. Wang, J. R. Hill and A. Day, "Vapor Grown Carbon Fiber/Phenolic Matrix Composites for Rocket Nozzles," presented at the AFOSR Polymer Matrix Composite Program Review, May 19-20, 2000, Courtyard Marriott, Long Beach, CA (abstract, p. 14).
3. R. Patton, C. U. Pittman, Jr., L. Wang, J. R. Hill and A. Day, "Vapor Grown Carbon Fiber/Phenolic Matrix Composites for Rocket Nozzles and Heat Shields," Advanced Material Processing Conference, sponsored by NASA, Huntsville, AL, September 2000.
4. C. U. Pittman, Jr. L. Wang and R. D. Patton, "Vapor Grown Carbon Fiber/Organic Matrix Composites: General Principles and Application to Erosion Resistant Rocket Nozzle Materials," 45th International SAMPE Symposium (SAMPE 2000), May 21-25, 2000, Long Beach, CA.
5. C. U. Pittman, Jr., "Chemical Incorporation of POSS[®] Derivatives into Crosslinked Polymer Matrices," POSS Nanotechnology Conference (sponsored by, Air Force Research Laboratory, EAFB and Hybrid Plastics), September 26-28, 2002, Huntington

Beach, CA.

6. C. U. Pittman, Jr. L. Wang, H. Ni and G. Z. Li, "Hybrid Organic Resin/POSS and Resin/Carbon Nanofiber Composites," Invited Lecture, 225th National Meeting of the American Chemical Society (Materials Chemistry Secretariat, Symposium on Hybrid Materials), New Orleans, LA, March 23-28, 2003.
7. C. U. Pittman, Jr., G. Z. Li and H. Ni, "Hybrid Inorganic/Organic Crosslinked Resins Containing Oligomeric Silsesquioxanes," IUPAC/Canadian Chemical Society Meeting, Ottawa, Canada, August 10-15, 2003 (Also published in *Macromolecular Symposia* (Wiley VCH)).

Theses/Dissertations Sponsored, in part, by Grant No. F49620-99-0191

1. Hanli Ni, MS Chem., 2002
2. Jun Xu, MS Chem., 2003
3. Xiaoming Xu, PhD, Chem. Eng., 1999
4. Jean Hill, MS Mech. Eng., 2001

Postdoctoral Scientists Supports, in part, by Grant No. F49620-99-0191

1. Lichang Wang
2. Gui Zhi Li

Key Results

1. DCPD (mpt. 39 °C) is made liquid by adding small amounts of cyclopentadiene or norbornene so it can be mixed and blended with other phases at room temperature or below.
2. DCPD/VGCF liquid suspensions were made with up to 10 wt% VGCF. These could be easily cured in molds.
3. When the wt% VGCF exceeded 15-22 wt% (depending on the class of fibers) it became difficult to make pastes because the consistence became like that of fibers and not a continuous viscous liquid medium due to the high fiber surface area per unit weight. Paste-like materials could be made in the 8-20 wt% range and cured.
4. More viscous liquid resins, particularly epoxies and phenolics could be blended with VGCF in higher shear mixing devices like two-roll mills, Brabenders and twin-screw extruders and then cured.
5. VGCF serve as reinforcing fibers, increasing in the moduli of all resin systems tested. However, strength increases do not always occur due to a combination of factors such as (1) 3-dimentional random alignment (2) packing fraction limitations (3) voids can be introduced at wt% of 20% or above, even after using extensive high shear blending.
6. The theoretical packing fraction limit of the VGCF is in the region of 20-26 wt%. Therefore, unless the average alignment can be increased, voids will always appear when the fiber fraction is increased. This is the most serious limitation of using VGCF.
7. Higher fiber wt% VGCF/phenolic composites were produced with extensive high shear mixing and curing under high pressures. These materials had exceptional high

temperature erosion resistance in plasma torch testing carried out at Thiokol (Huntsville, AL). The ability to withstand 400 to 800 BTU/ft² sec plasma torch heating (1650 °C) was examined as a function of fiber volume fraction, V_f . Samples with 35-40% VGCF had erosion rates almost as low as NASA's standard Space Shuttle Reusable Solid Rocket Motor (RSRN) nozzle (carbon cloth/phenolic composite). This remarkable result was at first surprising. The torch's flame generated a large lateral red glowing region on the VGCF/phenolic surface which caused surface graphitization. However, the very short fibers provided a very short heat conducting pathway perpendicular to the surface. Thus, heat transfer into the sample was slower than that of the RSRM nozzle composite (with continuous carbon fiber). This led to (a) less thermal expansion (b) less subsurface chemical reaction and outgassing. While these materials are electrically conducting, the composites are not good thermal conductors.

8. EMI shielding studies found that VGCF/vinyl ester composites exhibited excellent high frequency electromagnetic shielding (J. Xu, MS Thesis; being written for publication). EMI shielding varied with the type of VGCF used, the fiber concentration, oxidation of the fiber surfaces and fiber diameter.
9. The electrical conductivity of VGCF/vinyl ester resins was studied. The resistivity dropped rapidly between 2 and 3.5 wt% VGCF (percolation limit reached), showing VGCF is far more effective than carbon black for antistatic or conducting composite uses. Remarkably, fibers which had been surface oxidized in HNO₃ at 115 °C (surface oxygen increased from 6% to 20%) behaved entirely differently, even though they were indistinguishable from unoxidized fibers by TEM and SEM. Their incorporation into vinyl ester composites gave insulating materials at 7 and 15 wt% (far above the percolation limit).
10. VGCF/isocyanate liquid resin mixtures were prepared and coated onto steel coupons followed by curing. Various wt% VGCF coatings were made. They are being studied now for corrosion resistance in chloride salt solutions to see if the reduced resistivity of the coating affords any corrosion protection.
11. Mixing VGCF into a preexisting EPDM resin via twin screw extrusion generated a composite which was used as a rocket motor liner for a solid propellant test motor. Test firing (Edwards AFB) demonstrated that VGCF mats remained, which protected the motor casing even after the EPDM resin had burned away. This is a significant result because it could lead to thinner, lighter liners which could reduce weight and increase either range or payload.
12. A tetraepoxy-tetra- β -styrylPOSS monomer prepared at Edwards AFB was blended with a low viscosity aliphatic epoxy resin and cured thermally. Various amounts of POSS were incorporated. These POSS/epoxy nanocomposites were evaluated (bending moduli, T_g, impact strengths etc.) TEM studies did not reveal any POSS aggregation, suggesting molecular dispersion of the POSS occurred during the cure. The POSS incorporation improved the properties of these resins at temperatures above T_g.
13. The same POSS monomer (item 12 above) was incorporated into vinyl ester (50% styrene) resins at various wt%. The resulting nanocomposites exhibited partial phase aggregation of the POSS (5 to 100nm POSS-rich regions) and some molecular

dispersion of POSS (TEM, EELs, EDX). All of the incorporated POSS was part of the polymer network.

14. Several dual nanophase composites were made which contained a POSS monomer and VGCFs. Some phenolic resins, cured after blending both POSS and VGCF, had essentially no observable T_g values and others had high T_g s. The combination of both nanophases led to exceptional high temperature mechanical properties (e.g. high E' values from 250-320 °C. We were unable to test beyond this range due to instrumentation limits). POSS/VGCF/vinyl ester and POSS/VGCF/DCPD nanocomposites were made. This appears to be an extremely promising area for future studies (related systems are now being examined as liner materials for rocket motors).
15. A number of semiinterpenetrating polymer networks (SIPNs) were prepared very simply with commercial linear poly(vinyl chloride) and thermosets such as isocyanates, epoxies and vinyl esters and then these were characterized. These systems were going to be used as baseline models. The same SIPNs were going to be prepared with 5 and 10 wt% of VGCF added. However, once the VGCF was added, true SIPN/VGCF composites did not result. A key problem encountered was the dispersion/denesting of the tangled VGCF in the viscous thermoplastic/thermoset matrices.